Liberation of selenium from alteration of the Bowland Shale Formation: evidence from the Mam Tor landslide

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Abstract: The Bowland Shale Formation is anomalously rich in selenium (Se) at levels an order of magnitude greater than other black shales. The Mam Tor landslide, Derbyshire, England, offers an opportunity to measure whether the Se anomaly is conferred to the alteration products formed by oxidative water flow through the shale. Selenium in the shale is concentrated in diagenetic pyrite. Alteration of the shale causes decomposition of the pyrite to iron oxyhydroxide, which is carried in colloidal form (ochre) by springs draining the landslide. The iron oxyhydroxide contains anomalously high Se, and anomalously high Se was measured in water ponded where the ochre precipitated, although not in flowing groundwater. Other trace elements including cadmium and thallium also occur at concentrations higher than in other ochres. Given the widespread nature of the Se anomaly in the Bowland Shale Formation and equivalents across Britain and Ireland, any alteration products derived from workings through the shale should be disposed of with care.

The Upper Carboniferous (early Namurian) Bowland Shale Formation consists of hemipelagic–pelagic shale deposited across central Britain and Ireland (Andrews 2013; Newport *et al.* 2018). To the north it passes into successions dominated by shallow water limestone and coal. The shale is dark grey to black, reflecting organic carbon concentrations of up to several per cent (Parnell *et al.* 2016; Fauchille *et al.* 2017), and thus a potential source of hydrocarbons (Andrews 2013; Gross *et al.* 2015; Hennissen *et al.* 2017). The shales are in the early oil window (<100°C) in central England, but are more thermally mature to the west and metamorphosed to slate in southern Ireland. Low permeability values (Cai & Ofterdinger 2014; Ma *et al.* 2016) enhance the potential to retain gas. The shale is variably pyritic and believed to be a source of metals into mineralizing fluids in northern England (Jones *et al.* 1994). The formation contains anomalously high concentrations of Se across the region (Parnell *et al.* 2016). A mean concentration of 21.5 ppm Se was determined from measurements of the shale from western Ireland to Lancashire, although subsequently whole-rock concentrations up to 80 ppm Se have been recorded in the shale in Ireland (authors' unpublished data). The occurrence of high concentrations across a range of thermal maturity suggests that the Se was incorporated from seawater during early diagenesis, rather than during burial. These concentrations are 1–2 orders of magnitude greater than a global mean shale concentration of 0.6 ppm Se (Turekian & Wedepohl 1961), which is itself greater than the contents in most sedimentary rocks. Even metalliferous black shales normally have Se concentrations an order of magnitude lower than the Bowland Shale Formation values (Mitchell *et al.* 2012). Given that high concentrations of Se in the environment can present problems owing to Se toxicity (Fordyce 2013), and that in most cases this derives from rocks with Se concentrations <5 ppm (see below), the much higher concentrations in the Bowland Shale Formation merit attention. The potential for Namurian shales to release unwanted Se to the environment is well known in Ireland, where livestock have been exposed to toxic

concentrations (Fleming & Walsh 1957; Rogers *et al.* 1990), but this has not yet been an issue in Britain.

The Se in the Bowland Shale Formation resides predominantly in pyrite (Parnell *et al.* 2016), and so is liable to be released upon oxidation of the pyrite during weathering. The high pyrite content of the Bowland Shale Formation has led to the formation of iron oxyhydroxide, sulphuric acid and other weathering products such as jarosite and gypsum, where water has flowed through it and oxidized the pyrite, in hillside stream sections, coastal cliff sections and in quarry waste piles. Iron oxyhydroxide (ochre) precipitates as a result of oxidation in water courses and other surface environments, where it can act as a sink for Se and other trace elements (Sapsford *et al.* 2015; Abed *et al.* 2017). There is, therefore, the potential for Se to be concentrated in alteration products from the Bowland Shale Formation. An opportunity to test this is afforded by the Mam Tor landslip, Derbyshire, where the Bowland Shale Formation (formerly known in this area as the Edale Shale) has been altered by water flow through the landslip to leave deposits of ochre, on a scale of cubic metres, at surface discharge sites.

The geology of Mam Tor (Hope Valley, Derbyshire, UK, National Grid Reference SJ 133834) consists of turbidite sandstones (Mam Tor Sandstone) above black pyritic hemipelagic shales (Bowland Shale Formation: Allen 1960; Banks *et al.* 1996; Banks 1997). Over 3000 years ago a landslide was initiated, which is still active (Vear & Curtis 1981; Skempton *et al.* 1989). The landslide forced the closure of the A625 between Sheffield and Manchester across Mam Tor in 1979. Near-surface groundwater drains down through the landslide, oxidizing the pyrite and emerging as acidic, ochre-precipitating springs (Vear & Curtis 1981; Steward & Cripps 1983; Banks *et al.* 1996; Adams *et al.* 2007). There have been several studies on the water chemistry, whole-rock geochemistry and mineralogy of the shales, the acidic and ferruginous water runoff, and the associated ochre and gypsum precipitates (Allen 1960; Smith *et al.* 1967; Spears & Amin 1981; Banks *et al.* 1996; Banks 1997; Adams *et al.* 2007). Fe concentrations show a

qualitative correlation with sulphate, suggesting that pyrite oxidation to iron oxide and sulphuric acid is occurring, and the Mam Tor waters have a pH of between 3.1 and 3.7 (Vear & Curtis 1981; Banks *et al.* 1996; Banks 1997).

This study investigates the following: (1) if the Mam Tor ochres have anomalous Se concentrations, reflecting the anomalous concentrations in the parent shales; (2) how the Se concentrations in Mam Tor ochres compare with those in other ochres; (3) whether any Se enrichments in ochres are associated with enrichments in selected other elements; (4) how the Se concentrations in Mam Tor ochres compare with the Se concentrations of rocks that give rise to environmental problems elsewhere.

Methods

Sampling spanned elevations from *c.* 400 m to *c.* 280 m (Fig. 1). At the highest level, a spring emerges from the head scar above a fault. Three samples of ochre were collected from a region of slipped blocks above the upper road, and the remaining samples are from a debris-flow region further down the slope, below the upper road (Fig. 1). Samples of shale were collected from within the landslide,

where it is visibly altered to varying degrees, and from beyond the landslide, where it is unaltered, including from an undisturbed section at Edale village (Stevenson *et al.* 1971). Bulk analyses of the ochre and shale samples (Table 1) were made after multi-acid digestion (perchloric, nitric, hydrofluoric and hydrochloric acids) by inductively coupled plasma mass spectrometry (ICP-MS). In addition to Se, measurements were also made of arsenic (As), cadmium (Cd) and thallium (Tl) in the ochres, as these elements have an affinity for iron oxide but can be a cause of environmental pollution. Pyrite in the fresh shale from Edale village was analysed by laser ablation (LA)-ICP-MS. Details of the ICP-MS and LA-ICP-MS techniques have been given by Parnell *et al.* (2017). Water was sampled from three sites in the spring and stream system (Fig. 1).

Results

Ochres at Mam Tor are predominantly orange–red in colour, with lesser quantities of white ochre. The ochres analysed were orange–yellow powders, sieved to exclude coarse particles (above 125 μm) before milling, consisting particularly of quartz, goethite, hematite and gypsum. Variations in colour reflect the different abundances of gypsum compared with hematite (red) and goethite (orange–yellow), with white ochres containing more gypsum.

The shales are black mudrocks with a bedding-parallel fabric along which they split. None of the samples was conspicuously fossiliferous. They consist predominantly of quartz, illitic clay and organic matter. Eight samples of shale contain 4.1–40.5 ppm Se, and a mean concentration of 18.4 ppm Se (Table 1). Excluding two samples that are conspicuously weathered to a rusty appearance, and likely to be leached, the mean concentration is 23.1 ppm Se.

Measurement of 11 samples of ochre gave a range of 1.0–7.2 ppm Se, and a mean concentration of 5.0 ppm Se. Low Se concentrations (1.0–2.0 ppm) occur in the ochre samples from the upper part of the landslide, in the region of slipped blocks. Higher concentrations (5.5–7.2 ppm) occur in the lower, debris-flow, region. Concentrations of As, Cd (Fig. 2) and Tl follow this general pattern.

Measurement of three samples of spring water gave a single concentrations above the detection limit of 0.2 mg kg^{-1} Se, at 1.72 mg kg^{-1} Se, measured where the water is ponding between the slipped blocks and the debris field, in the same area as the most Se-rich ochres.

LA-ICP-MS mapping showed that Se residence is strongly concentrated in crystals of pyrite (Fig. 3). Measurements of the pyrite yielded a mean composition of 31 ppm Se and 130 ppm As, and local concentrations up to 80 ppm Se and 250 ppm As.

Discussion

Anomalous Se in Mam Tor alteration products

The Se content of the ochres is greater than in most other measured ochres. Most ochres in drainage systems from coal mines, derived from the oxidation of pyrite in coal and mudrock, in the UK contain <0.5 ppm Se (Fig. 4; Coal Authority, unpublished data). Published analyses of ochres usually record Se at below the detection limit (Sapsford *et al.* 2015; Hedin 2016). Natural ochres of non-specific origin, used as pigments and studied by the archaeological community, similarly have Se contents of about 1 ppm or lower (Green & Watling 2007; Iriarte *et al.* 2009). The Mam Tor ochres are, therefore, anomalous for their high Se concentrations relative to all measured ochre deposits. This reflects the high Se concentrations in the Bowland Shale Formation protolith.

The mean concentrations of As, Cd and Tl in Mam Tor ochres are 16.7 ppm, 13.9 ppm and 3.5 ppm respectively. The concentrations of trace elements in the ochres are consistently higher in the lower part of the landslide (Fig. 2), where the water becomes ponded.
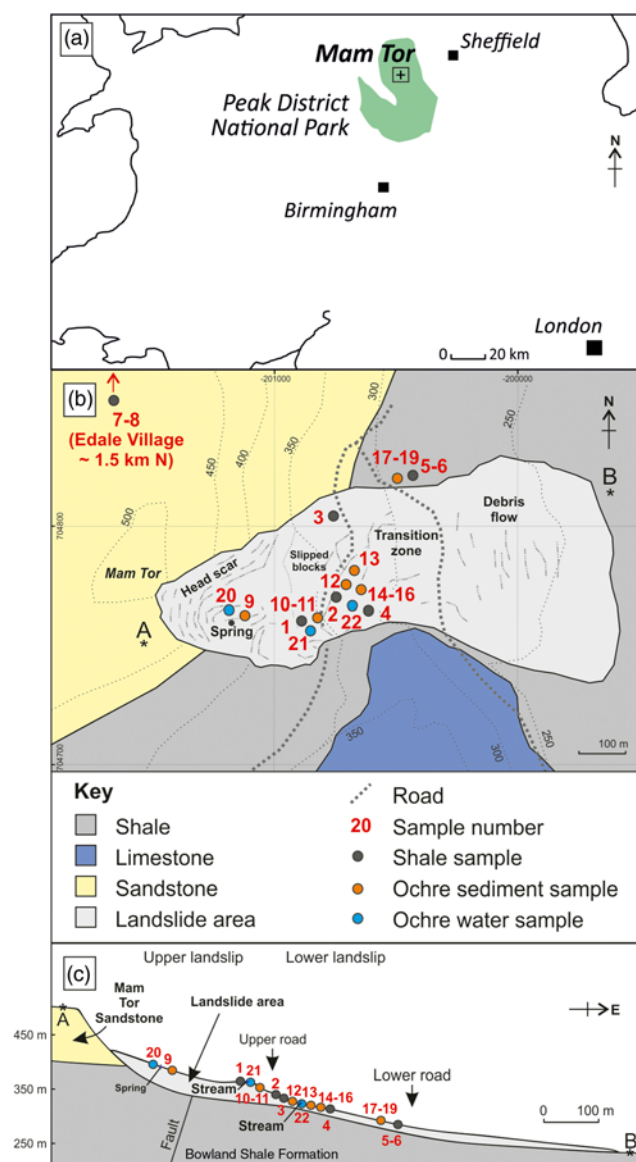

Fig. 1. Location maps and cross-section through Mam Tor landslide (after Waltham & Dixon 2000), showing context of samples.

Table 1. *Mineral, whole-rock, ochre precipitate and water compositions for Mam Tor samples*

Sample type	Map ID	Fe (%)	S (%)	Se (ppm)	As (ppm)	Cd (ppm)	Tl (ppm)
Edale pyrite		23.1	–	30.7	130.5	–	–
Shale	1	4.8	5.6	4.1	71.1	0.6	0.4
Shale	2	0.5	0.1	4.3	6.9	0.1	0.1
Shale	3	1.6	2.0	4.6	40.0	0.3	0.1
Shale	4	3.9	4.3	20.9	38.0	2.5	0.7
Shale	5	6.9	0.2	40.5	86.5	0.8	0.8
Shale	6	6.7	0.2	39.6	85.7	0.7	0.8
Shale	7	4.5	3.6	15.5	21.4	3.4	0.4
Shale	8	6.1	5.1	17.9	29.3	3.4	0.7
Mean shale		4.4	2.6	18.4	47.4	1.5	0.5
Median shale		4.7	2.8	16.7	39.0	0.8	0.5
Ochre sediment	9	39.0	3.5	1.0	7.6	0.03	0.2
Ochre sediment	10	40.7	2.4	2.0	7.6	0.05	0.2
Ochre sediment	11	40.4	2.4	1.9	8.3	0.04	0.1
Ochre sediment	12	2.3	4.3	5.5	8.1	2.5	0.2
Ochre sediment	13	9.5	0.3	6.3	25.5	12.9	0.5
Ochre sediment	14	17.2	0.5	7.2	28.4	21.1	0.7
Ochre sediment	15	2.1	0.9	6.4	14.6	6.5	0.4
Ochre sediment	16	11.2	1.6	5.6	37.8	3.5	0.6
Ochre sediment	17	15.6	1.0	6.4	17.9	44.7	15.1
Ochre sediment	18	15.5	1.0	6.3	17.6	43.9	15.1
Ochre sediment	19	15.2	1.3	6.6	10.7	18.0	5.1
Mean ochre sediment		19.0	1.7	5.0	16.7	13.9	3.5
Median ochre sediment		15.5	1.3	6.3	14.6	6.5	0.5
		Se (ppb)	As (ppb)	Cd (ppb)			
Ochre water	20	<LOD	<LOD	5.24			
Ochre water	21	<LOD	<LOD	1.53			
Ochre water	22	1.72	1.1	2.05			

Water LOD (level of detection): As, 0.97 ppb; Cd, 1.99 ppb; Se, 1.59 ppb.
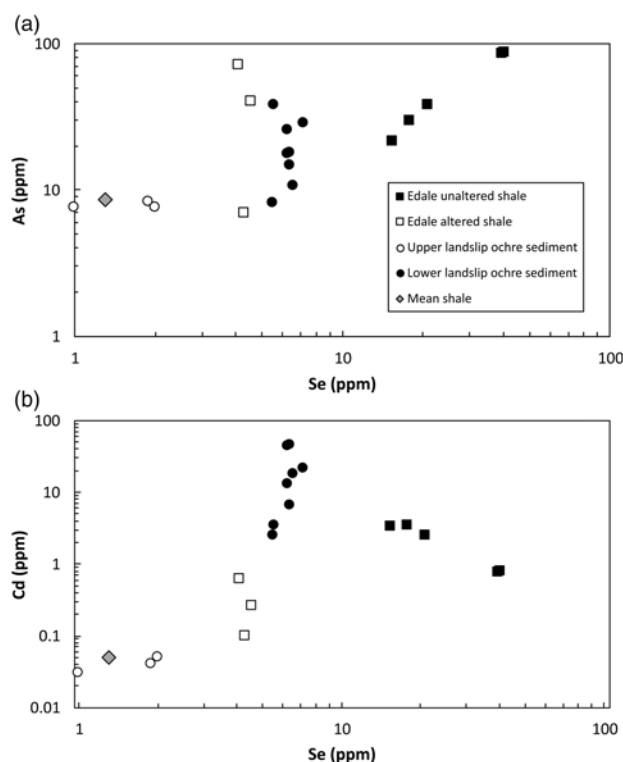

Fig. 2. Cross-plots of (**a**) Se and As, (**b**) Se and Cd for samples of Bowland Shale Formation and ochres at Mam Tor. Altered samples of shale show depletion of elements. Ochres are enriched in Cd relative to parent shales. All data are anomalous relative to global mean shale concentrations (from Rudnick & Gao 2003; Hu & Gao 2008; Stüeken et al. 2015).

Concentrations of Se in the ochres are about one-third of the concentrations in the parent rock, but are still high because the concentrations in the shale are so much greater than in most other rocks. The mean As concentrations of ochre is similarly about one-third of that in the shales (mean 47.4 ppm). In contrast, the concentrations of Cd in the ochres are much higher than in the parent shale (mean 1.5 ppm), although Cd concentrations an order of magnitude greater have been measured in the Bowland Shale Formation further north (Lepp 1981; Mislin & Ravera 1986). The natural enrichment of Cd is comparable with experimental data, which show Cd to be the most enriched metal in ochre in a multi-element study (Abed et al. 2017).

The ready adsorption of As, Cd and Tl has led to the application of ochres and iron oxides to sequester these elements out of groundwaters (Doi et al. 2005; Abed et al. 2017; Li et al. 2017). The As concentration in the Mam Tor ochre is higher than concentrations in some ochres from UK coal mines (Dobbie et al. 2005; Olimah et al. 2015), but not in others (Sapsford et al. 2015) or in ochres elsewhere (e.g. Bowell & Bruce 1995; Cravotta 2008; Valente et al. 2011), but is nonetheless above the crustal mean concentration of 5.7 ppm. Soluble forms of both Se and As are adsorbed strongly onto iron oxides in acid conditions (Manning et al. 1998; Su & Suarez 2000), as pertain in waters draining through pyritic shales. The mean Cd concentration in the ochres is above concentrations previously reported in ochres (Fuge et al. 1994; Hammarstrom et al. 2003; Dobbie et al. 2005; Iriarte et al. 2009; Sapsford et al. 2015). The mean Tl concentration of the ochre is also higher than the few concentrations recorded previously for ochres (Iriarte et al. 2009; Sapsford et al. 2015). Notably, As and Cd concentrations are also well above soil guideline value (SGV) levels (Environment Agency 2009a,b). The anomalous concentrations are of interest as even small volumes of ochre, if dried out, can become a
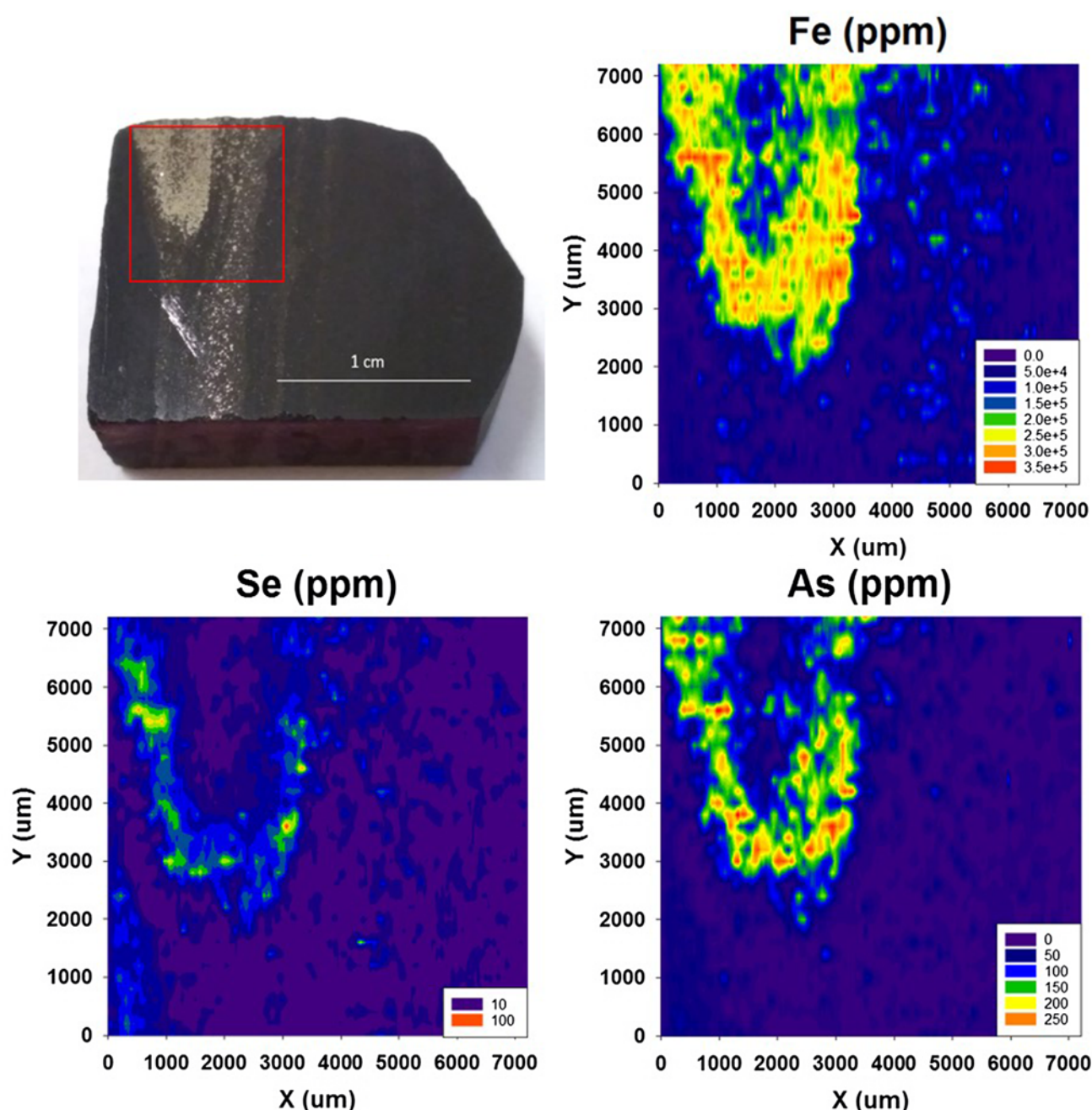
Fig. 3. LA-ICP-MS map for Fe, Se and As in Bowland Shale Formation sample, including a concentration of pyrite. Se and As are preferentially distributed within the pyrite.

source of wind-blown contamination, as occurred in a residential region of Anglesey near a former copper mining site (Isle of Anglesey County Council 2010).

The concentration of 1.72 mg kg^{-1} Se in the ponded water is also anomalously high. For comparison, this is above a mean concentration of 0.4 mg kg^{-1} Se in 32 water samples in groundwaters in Manchester and East Cheshire, immediately to the west of the study area (Griffiths *et al.* 2003), and above all concentrations measured in groundwaters measured in the East Midlands to the east (Smedley & Edmunds 2002). However, two other samples of spring water contained less than 0.2 mg kg^{-1}, indicating that there is no evidence of a Se anomaly in flowing groundwater.

Selenium residence

The residence of Se in the pyrite within the shale indicates that the Se is likely to be mobile once the shale becomes weathered and the pyrite is oxidized. Whereas sulphur liberated from altered pyrite is highly mobile as sulphuric acid, some Se may occur in elemental form or as selenide ions. These Se species can be adsorbed onto iron oxide (Balistrieri & Chao 1990; Rovira *et al.* 2008), so there is potential for retention of Se on the ochres resulting from pyrite oxidation. A combination of fine particles, high surface area and the affinity of iron oxides for Se and other trace elements makes ochres a natural trap for groundwater solutes. Ochre has even been deployed to extract Se from waters draining through coal waste (Donovan & Ziemkiewicz 2013). The situation at Mam Tor is very similar, where ochres are precipitated from, but also extracting Se from, the waters draining through the landslipped shale.

Potential pollution at high Se concentrations

The anomalously high nature of the ochre Se concentrations can be put into context by comparison with the Se concentrations of rocks
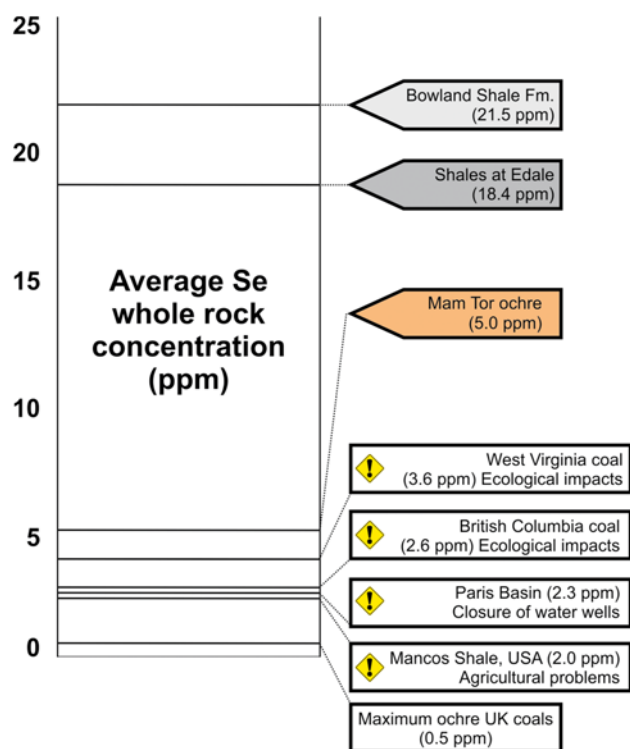
Fig. 4. Mean concentrations of Se in Bowland Shale Formation and Mam Tor ochre samples, in comparison with concentrations for other rocks regarded as problematic for the environmental consequences of their Se, and low contents in ochres associated with UK coals. Sources are given in the text.

that are regarded as problematic because of their Se (Fig. 4), and that have experienced comparable burial histories to depths of a few kilometres. The mean concentrations of coal in West Virginia, and Elk Valley, British Columbia, both of which are held responsible for environmental contamination by Se, are 3.6 ppm Se (Vesper *et al.* 2008) and 2.6 ppm Se (Kennedy *et al.* 2015) respectively. The mean concentration of shale held responsible for Se contamination of water supply in the Paris Basin, and consequent closure of water wells (Cary *et al.* 2014), is 2.3 ppm Se (Bassil *et al.* 2016). The mean Se concentration of the Cretaceous Mancos Shale, a cause of widespread environmental concern for agriculture, water supply and endangered aquatic species in southwestern USA, is cited as 1.1 ppm Se (Tuttle *et al.* 2014) and 2.0 ppm Se (US Department of Energy 2011). The mean concentration of Se in the Mam Tor ochres exceeds all of these concentrations from other regions where they give rise to environmental problems.

Although the Se concentration of the shale is an order of magnitude above that in typical shales, it is in the lower half of the range of concentrations measured in the Bowland Shale Formation equivalents across Britain and Ireland (Parnell *et al.* 2016). The highest concentration that we have measured is 80 ppm Se in County Cork, Ireland, about four times that of the mean concentration of the shale tested from Mam Tor. These data imply that alteration of the Bowland Shale Formation elsewhere could yield alteration products that are more loaded with Se than at Mam Tor, and potentially more hazardous.

Conclusions

Analysis of the ochres (iron oxyhydroxide deposits) from the Mam Tor landslide shows that they contain elevated concentrations of Se, relative to crustal mean concentrations and ochres elsewhere. The high concentrations of Se and other toxic elements including As, Cd and Tl in the ochre are attributed to the elevated concentrations

recorded in the Bowland Shale Formation, which would have released iron oxide and trace elements upon oxidation of the pyrite content. The mean Se concentration of the ochres is greater than that in rocks that have caused environmental problems elsewhere. The ochres at Mam Tor are volumetrically very limited, and the waters draining Mam Tor are not used for public supply, so do not constitute a hazard, but the data indicate the need for caution in any large-scale working of the Bowland Shale Formation in Britain and Ireland.

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